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REVIEW: LIGHT-INDUCED YELLOWING OF LIGNOCELLULOSIC PULPS – MECHANISMS AND PREVENTIVE METHODS

Magnus Paulsson [a,b,*] and Jim Parkås [c]

This review will focus on recent progress regarding the mechanisms of light-induced discoloration of mechanical and chemimechanical pulps and on the proposed preventive treatments. It is evident that the mechanisms behind photoyellowing of lignin-rich pulps are complex and that several types of reaction pathways may coexist. Photoyellowing proceeds via one initial fast phase and a slower following phase. The fast phase has been ascribed to oxidation of free phenolic groups and/or hydroquinones and catechols to photoproducts of mainly quinonoid character. A multitude of reactions involving several lignin subunits are possible. Important intermediates are phenoxyl radicals, and to some extent ketyl radicals. The importance of the phenacyl aryl ether pathway might be more important than previously thought, even though the original content of such groups is low in lignin. Even though many preventive methods against photoyellowing have been suggested, no cost-efficient treatment is available to hinder photoreversion of lignin-containing paper permanently. Suggested methods for stabilization include chemical modification (etherification and esterification), coating the paper product, addition of radical scavengers, excited state quenchers, or ultraviolet absorbing compounds.

Keywords: Chemimechanical pulp; Discoloration; Light-induced; Lignin; Mechanical pulp; Stabilization; Yellowing

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This paper is dedicated to the memory of Professor Knut Lundquist.

INTRODUCTION AND SCOPE OF THE REVIEW

Enhanced production and efficient utilization of lignocellulosic products are issues of critical importance to both industry and society. Lignin-containing, high-yield mechanical and chemimechanical pulps such as stone ground wood (SGW) pulp, thermomechanical pulp (TMP), and chemithermomechanical pulp (CTMP) have a number of advantages when compared with chemical pulps. Examples of such advantages are the efficient utilization of the available virgin fiber resource and the possibility to produce pulps with a unique combination of light scattering, bulk, and strength properties that render it possible to produce high-quality and low basis weight printing papers at a low cost (Höglund and Wilhelmsson 1993; Heikkurinen *et al*. 2009). The main unresolved problems associated with the aforementioned pulp types are the high electrical refining energy needed for fiber separation and development of properties and the inferior brightness and brightness (color) stability that occurs upon exposure to daylight or indoor illumination. The latter hinders high-yield pulps being used as the major fiber component in long-life, high-quality paper (and board) products. Therefore,

mechanical and chemimechanical pulps are currently used in short-life graphical paper qualities such as newsprint, and uncoated and coated magazine papers. Newsprint production has decreased by about 20% since the year 2000 (Fig. 1) and it is likely that this decrease will continue due to rapidly changing use of media, altered reading habits, and competition from electronic publications. Alternative value-added products from high-yield pulps are therefore needed, and it is likely that these products, *e.g.*, fine paper, require that the lignin-containing pulps have improved brightness (color) stability, especially if these pulps are to be used as the main fiber component.

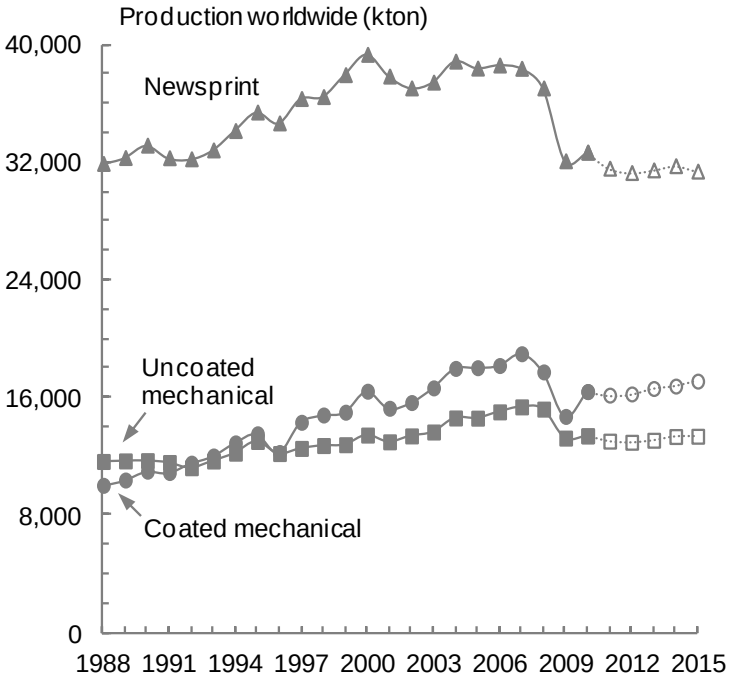

Fig. 1. The production and production forecast of wood-containing graphic papers worldwide (source: RISI)

Light-induced discoloration has been extensively studied since the mid-20th century and is one of the most studied wood chemistry problems. Extensive research efforts in North America and Europe during the 15 years starting from the beginning of the 1990s were devoted to this recalcitrant problem. The vast amount of new information is reflected in the number of scientific journal and conference articles published in this time period (Fig. 2). The research activities have, however, declined since then, and it is reasonable to expect that more efforts are needed in the future if the utilization of lignin-containing pulps is going to be extended.

Brightness (color) reversion, also known as yellowing, discoloration, or ageing, of pulp and paper products can be caused by several factors *e.g.*, light, heat (Gellerstedt *et al*. 1983; McLellan *et al*. 1990; Paulsson and Ragauskas 1998a), or air pollution (Adelstein *et al*. 2003). A number of excellent reviews dealing with various aspects of these phenomena have previously been published (Gratzl 1985; Heitner 1993; Leary 1994; Davidson 1996; Forsskåhl 2000; Lanzalunga and Bietti 2000; Heitner 2010).

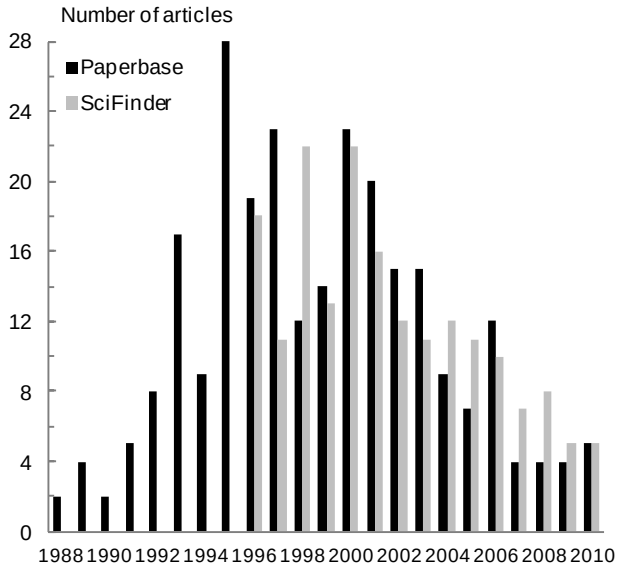

Fig. 2. The number of journal and conference articles in the databases Paperbase (1988-2010) and SciFinder (1996-2010) dealing with light-induced discoloration of lignocellulosic materials

The scope of this review is to focus on the progress regarding the light-induced discoloration of mechanical and chemimechanical pulps and to discuss the underlying mechanisms for the color formation of these pulps. Further, an overview of the preventive photostabilizing treatments proposed will also be given.

EARLY REPORTS OF LIGHT-INDUCED YELLOWING

The rapid discoloration of groundwood-based papers was reported as early as the end of the 19th century by Cross (1897) and Evans (1898), and it was concluded that oxygen participates in the discoloration process. A few years later, Klemm (1903) introduced light as a contributing factor, and it was also early proposed that the discoloration was due to an oxidation of the non-cellulosic constituents in the pulp such as fats, waxes, resins, and lignin (Sindall 1920) and that papers made from chemical pulps were more stable compared to papers produced from mechanical pulps (Schoeller 1912). Further, in many of the early observations, rosin and iron were said to be important factors that influenced the extent of discoloration of both chemical and mechanical pulps. The chemical changes associated with the discoloration and degradation of lignin and lignocellulosic materials were first studied in the 1940s. Irradiation of Brauns' lignin and spruce woodmeal with ultraviolet (UV) radiation generated light-absorbing compounds, and lignin underwent chemical changes that were reflected in lower methoxyl and Klason lignin contents (Forman 1940). Vanillin (one of the products of lignin degradation) underwent a rapid discoloration when irradiated in solution and caused extensive yellowing of impregnated filter paper. Demethoxylation of lignin was later reported for irradiated milled wood lignin (MWL) (Sjöholm *et al*. 1992), groundwood-based papers (Lewis and Fronmuller 1945; Leary 1967; Hemmingson and Morgan 1990), jute (Callow and Speakman 1949), and radiata pine wood (Sinclair and Vincent 1964). Light-induced ageing of groundwood pulp in different atmospheres showed that atmospheric oxygen

increased the discoloration rate and consequently that oxygen participates (directly or indirectly) in chromophore formation (Nolan *et al*. 1945; van den Akker *et al*. 1949). It was also found that discoloration was accelerated by an increased temperature. Further, the discoloration was not directly proportional to the irradiation time, and most of the chromophore formation occurred rapidly during irradiation (Lewis *et al*. 1945; Francis *et al*. 1991; Ek *et al*. 1992). The initial phase was followed by a slower, less detrimental phase. Nolan *et al*. (1945) stated that the photochemical reactions were of at least two types: 1) discoloration that occurs at wavelengths shorter than 385 nm and 2) bleaching by wavelengths longer than 385 nm. Efforts to find a photostabilizing treatment also began in the 1940s. Reineck and Lewis (1945) studied a large number (>100) of organic compounds as inhibitors for light-induced discoloration, but none of the studied compounds improved the stability to any noticeable extent. The early research did reveal that lignin is primarily responsible for the light-induced discoloration of groundwood pulps, that oxygen participates in the reactions, and that pH, moisture, and temperature influence the extent of reversion. A more detailed presentation of early research efforts is summarized in a number of review articles (Walton 1929; Spinner 1962; Kringstad 1969; Rapson and Spinner 1979).

FACTORS AFFECTING LIGHT-INDUCED YELLOWING

The wavelength distribution of the radiation that strikes a paper surface is of utmost importance for the extent of discoloration. Most of the ultraviolet component of sunlight that reaches the earth's surface has a wavelength between 293 and 400 nm. The total radiation energy at the surface of the earth in the 300 to 350 nm range is about one-third of that between 350 and 400 nm (Hirt *et al*. 1960). For photoyellowing reactions indoors, it is worth noting that ordinary window glass filters out most of the radiation below about 315 nm (Hirt and Searle 1967) and that office papers when subjected to only fluorescent light are exposed to no radiation below about 350 nm (McGarry *et al*. 2004). Different spectral regions of radiation are responsible for either yellowing (ultraviolet radiation) or bleaching (visible light), as already stated (Nolan *et al*. 1945; Leary 1967; Andtbacka *et al*. 1989; Forsskåhl and Janson 1991; Andrady *et al*. 1991; Andrady and Searle 1995). The transition between discoloration and bleaching is not fixed to a certain wavelength but is a function of the wood raw material, pulping process, and stabilizing treatment. For paper indoors, it is expected that the most extensive yellowing is obtained when sheets are subjected to radiation between 330 and 385 nm. The photochemical effect is a function of the absorption by the substrate (the Grotthus-Draper law), the efficiency of the photochemical process (the quantum yield), and the intensity and wavelength of radiation. The primary process of photochemistry includes the absorption of a photon by a molecule that activates (excites) the molecule, which in turn will lose its energy in different ways, *i.e.,* by heat, by fluorescence or phosphorescence, by chemical changes within the molecule, by breaking of chemical bonds (photolytic cleavage), or by transferring its energy to another atom or molecule. The secondary process (post-irradiation effects) is when the transfer of energy starts a chain of events, for example, the generation of singlet oxygen from an excited molecule and that singlet oxygen in turn oxidizing a chemical constituent. Factors such as temperature, amount of oxygen present, and humidity are normally not important for the primary process but can be essential for the secondary process and thus the outcome of the irradiation (Hirt *et al*. 1960; Feller

1994). Light-induced yellowing is largely a surface phenomenon, with about 50% of the discoloration occurring at a depth of about 20 μm (Forsskåhl *et al*. 1995). The depth of discoloration is, however, influenced by the wavelength of irradiation, and since many materials absorb more radiation as the wavelength decreases, the depth of penetration is lower at short wavelengths (Feller 1994). Continuous irradiation may also lead to different results compared to intermittent exposure (altering light and dark exposure), since the moisture content and temperature may be different (Launer 1948). Thus, the procedure (spectral distribution of the light source, humidity, air recirculation, temperature, *etc*.) chosen for studying the light-induced yellowing of lignocellulosic materials will have an influence on the outcome. For example, the irradiation source used has an influence on the severity of the initial phase of discoloration (Paulsson and Ragauskas 1998b). Previous investigations have shown the importance of choosing a light source that resembles the actual reversion situation as closely as possible, if realistic light-induced reversion results are to be obtained (Paulsson and Ragauskas 2000; Paulsson *et al*. 2002; McGarry *et al*. 2004, Fjellström *et al*. 2007a). This is especially true for chemically modified or additive-treated, high-yield pulps. The usage of non-standardized ageing conditions complicates the interpretation of the results reported in the literature both for mechanistic and photostabilizing studies. If an inadequate irradiation source and ageing setup is used, the type of deterioration obtained and the conclusions drawn from it will most likely have little relevance for the photochemical processes that occur when a paper is used under normal conditions. The influence of ageing method is not within the scope of the present review, and a deeper discussion of the problems associated with this will, with a few exceptions, not be discussed further.

Metal ions present in the pulp could influence the stability, both as directly involved in the reactions or as an enhancer of color by forming colored complexes with lignin and extractives (Gupta 1970; Polcin and Rapson 1972; Ni *et al*. 1999; Peart and Ni 2001). Transition metals such as ferrous, ferric, and copper ions especially aggravate light-induced discoloration (Janson and Forsskåhl 1989; Ni *et al*. 1998). Effects of pH on the extent of light-induced yellowing have also been claimed (Lewis *et al*. 1945) with maximum brightness stability at pH 3.0 to 4.5 for unbleached groundwood pulp. However, another study has shown that a somewhat higher pH (6.0) could be more beneficial (Gellerstedt and Pettersson 1977). On the other hand, more recent experiments could not verify this fact for highly bleached groundwood pulp (Andtbacka *et al*. 1989); no significant difference in the yellowing rate in the pH interval 2 and 10 was obtained (Holmbom 1988). However, it has been reported that acidic papers containing mechanical pulp are more prone to discoloration than alkaline papers (Bond *et al*. 1999, 2001; Forsskåhl and Tylli 2001). Light-induced discoloration is accompanied by acidification (Andrady and Searle 1995; Forsskåhl and Tylli 2001), which contributes to a reduced mechanical performance. Further, the extent of discoloration also depends on the prevailing humidity and temperature conditions during ageing. It is generally agreed that the presence of moisture will speed up discoloration (Nolan *et al*. 1945; Spinner 1962; Forsskåhl 1995), even though others have reported this effect to be minor (Andtbacka *et al*. 1989). The temperature will influence the relative humidity and the oxygen content of the atmosphere, and the temperature should be kept low during irradiation to minimize heat-induced discoloration.

Oxygen participates in the photoyellowing reactions even though its exact role has not been fully elucidated. Several studies have shown that an oxygen-free atmosphere only marginally changes the extent of reversion of lignin model compounds or lignin-

containing papers (Nolan *et al*. 1945; van den Akker *et al*. 1949; Weir *et al*. 1995a; Li and Ragauskas 2000; Paulsson *et al*. 2001), whereas others have shown that oxygen is important for the photodegradation of lignin and lignin model compounds, as well as for the formation of chromophores (Leary 1968a, b; Lin and Kringstad 1971; Fukagawa and Ishizu 1991). This indicates that atmospheric oxygen is not of sole importance for light-induced discoloration or that only a trace of oxygen is necessary to cause the discoloration (Andtbacka *et al*. 1989).

The wood species, pulping method, and bleaching characteristics have all been claimed to have an influence on the discoloration rate. Hardwood pulps that have lower lignin contents have been reported to be more photostable than softwood pulps (Janson and Forsskåhl 1989; Johnson 1989; Paulsson and Ragauskas 1998b; Fjellström *et al*. 2007a). The pulping method used will also affect the stability, and it has been proposed that mechanochemical changes of the lignin macromolecule can generate new photo-sensible structures (Wu *et al*. 1994; Johansson *et al*. 2002). Groundwood pulps that are subjected to lower temperatures during fiber release seem to be somewhat more photostable (Fjellström *et al*. 2007a). The results regarding the effect of sulfonation are more unclear; some studies have reported that softwood CTMPs are more photostable than softwood TMPs (Heitner and Min 1987; Johnson 1989), whereas others have reported the opposite (Gellerstedt *et al*. 1985; Agnemo *et al*. 1991; Tylli *et al*. 1992). Bleached high-yield pulps lose more brightness units during ageing than unbleached; (Forsskåhl 2000; Fjellström *et al*. 2007a), an effect that is partly due to the consequence of the Kubelka-Munk relationship and partly due to the generation of light-sensitive structures during lignin-retaining bleaching. The difference in photostability between oxidatively (hydrogen peroxide) bleached and reductively (dithionite, bisulfite) bleached pulps is not fully understood, and different opinions regarding the effect of reductive and oxidative bleaching exist (Jansen and Lorås 1968; Abou-State 1976; Janson and Forskåhl 1991; Janson 1993; Kuys and Abbot 1996; Forsskåhl 2000). The discrepancy in reported observations could be due to differences in exposure conditions, light sources, exposure times, grammage of the exposed samples, and procedures chosen for quantifying the color reversion (Schmidt and Heitner 1993a; Kimura *et al*. 1994; Paulsson and Ragauskas 1998b).

New proposed bleaching agents, such as sodium percarbonate and amineborane (Leduc *et al*. 2002), hydrogen peroxide additives such as tetra-acetyl-ethylenediamine (Agrawal *et al*. 2005; Hu *et al*. 2011), tetraalkylammonium salts (Hu 2003a), fluorescent whitening agents (Zhang *et al*. 2009a), a combination of reductive and oxidative bleaching (Petit-Conil and de Choudens 1994; Kuys and Abbot 1996; Pan 1999), or alternative alkali sources for hydrogen peroxide bleaching (Savoye *et al*. 2011) have been tested with very limited photostabilizing effects. A recent study in which different types of mechanical and chemimechanical pulps were subjected to accelerated or ambient ageing showed that neither the pre-treatment procedure (sulfite or alkaline hydrogen peroxide) nor the bleaching method (dithionite or hydrogen peroxide) altered the photostability in any decisive way (Fjellström *et al*. 2007a; Holmbom 1988). It is, however, evident that no matter how mechanical or chemimechanical pulps are produced, they undergo extensive photoyellowing. The difference is how rapid the discoloration occurs and since hardwood (especially aspen) pulps are more photostable, these pulps are the first choice for usage in high-quality, long-life products.

THE CHEMISTRY OF LIGHT-INDUCED YELLOWING

It is important to remember that much of the knowledge gathered related to the mechanism of light-induced yellowing originates from experiments where fairly simple lignin model compounds were irradiated in organic solvents. Despite the fact that important knowledge can be and has been gained by this approach, there are some drawbacks which must be acknowledged when evaluating and comparing results in the literature:

- A low molecular weight lignin model compound in solution does not fully simulate the same lignin functionality in a true ageing case, *i.e.* in solid state in the presence of carbohydrates and other lignin moieties.
- The supply of oxygen might differ between solution and solid-state experiments (solubility, diffusivity).
- The choice of solvent might influence the outcome of the reactions.
- The mobility of lignin units is different in a solution than in a restricted solid matrix, which is important when contact between different functionalities is needed for the reactions to occur or when a radical pair formed by homolytic bond cleavage separates.
- The lifetime of intermediate radicals could be different in solid state compared to in solution state.

In addition to these drawbacks in using simple lignin model compounds in solution, the intensity and spectral distribution of the irradiation source used often varies between different investigations in the literature. This might lead to different conclusions as discussed above. Due to the complexity of lignin and the challenges to analyze lignin in the solid state as in mechanical pulp or as an isolated lignin sample, work with simple lignin models has been and still is inevitable. Analysis of lignin in the solid state, *e.g.*, in wood or pulp, is difficult (due to its complex structure and interference from other wood components), and efforts to isolate lignin without affecting the chemical structure often results in low yield. Experiments performed by subjecting lignin model compounds to irradiation in solid state (adsorbed to filter paper or pulp sheets) might lead to low recovery yields due to oligomerization and reactions with the substrate. Even though this might better simulate a real ageing case, this approach is challenging from an analytical perspective.

The main mechanism of photoyellowing of lignin-containing materials as we know it today can broadly be divided into three stages:

1. Energy absorption [ultraviolet and visible (UV/VIS) radiation] by photo-active groups (chromophores) in the lignin.
2. Formation of intermediate structures, *e.g.,* phenoxyl radicals (several suggested mechanisms).
3. Formation of chromophores absorbing visible light from the initially formed intermediates.

In addition, other reactions, not necessarily involving phenoxyl radicals, could influence the formation of color and the photodegradation of lignin. The basic knowledge surrounding the mechanisms will be reviewed in subsequent sections.

Energy Absorption

The near-ultraviolet wavelength region of 300 to 400 nm of the sunlight spectrum is most important to light-induced yellowing, since:

- Radiation in this region is quite energy-rich ($E \propto \lambda^{-1}$) and capable of inducing significant photochemical changes.
- The amount of radiation below 300 nm reaching earth is low.
- Most lignin chromophores absorb radiation effectively in this region.

The main chromophores (here UV/VIS absorbing groups) in wood and mechanical pulps are lignin moieties of various kinds and, to some extent, certain extractives (Norrström 1969; Lorås and Wilhelmsen 1973). The main chromophoric groups in native wood lignin are various kinds of ring-conjugated ethylenic groups, such as cinnamyl alcohol and cinnamaldehyde groups together with carbonyl groups, such as α-carbonyl groups and quinones (Pew and Connors 1971; Imsgard *et al*. 1971; Hon and Glasser 1979; Gratzl 1985). In addition to the chromophores present in native wood lignin, the mechanical treatment of wood during the pulping process may cause mechanochemical changes in the lignin macromolecule. For instance, it might lead to an increase in α-carbonyl groups (and quinones) (Lee and Sumimoto 1990; Itho *et al*. 1993; Johansson *et al*. 2002) and the formation of UV/VIS-absorbing stilbenes from phenylcoumaran (β-5) and 1,2-diarylpropane units (β-1) (Lee *et al*. 1990; Wu *et al*. 1991). Also, the use of chemicals in an optional pre-treatment stage or in bleaching stages influences the distribution of chromophores and leucochromophores (precursors to colored groups) in the lignin. Examples of this phenomenon are reactions of enals and enones with sulphite during impregnation and pre-heating prior to refining (Gellerstedt *et al*. 1977; Suckling 1991; Lundquist *et al*. 2007), formation of stilbenes (Gellerstedt and Agnemo 1980a; Gellerstedt and Zhang 1992), and hydroquinones via Dakin-type reactions (from phenolic α-carbonylic structures) during hydrogen peroxide bleaching (Gellerstedt and Agnemo 1980b; Lee and Sumimoto 1991; Gellerstedt and Zhang 1992), and degradation of cinnamaldehyde end groups by hydrogen peroxide (Gellerstedt and Agnemo 1980b; Gellerstedt and Zhang 1992).

To some extent, alkaline hydrogen peroxide degrades quinones but could also induce hydroxylation of quinones, resulting in hydroxyquinones that are more stable against degradation (Gellerstedt *et al*. 1980; Abbot 1995; Svensson-Rundlöf *et al*. 2006). Further, metal ions, especially transition metal ions such as iron, can form strongly colored complexes with lignin moieties (*e.g.* phenols, catechols) and extractives (*e.g.* flavonoids) (Gupta 1970; Polcin and Rapson 1972; Ni *et al*. 1999; Peart and Ni 2001).

The main chromophoric groups in lignin-rich pulps are shown in Fig. 3 with their approximate absorption wavelength maxima. It is, however, important to know that the absorption maxima could be altered if the chromophoric group is in a solid lignicellulosic matrix. For example, it has been reported that the absorption bands of differently substituted *o*- and *p*-quinone model compounds were intensively red shifted (by 30 to 150 nm) when impregnated onto lignin-rich pulp (Zhang and Gellerstedt 1994a). Further, it has also been suggested that phenoxyl radicals, which are known to be very stable in a solid matrix (days), could act as chromophores, absorbing energy in the range of 370 to 410 nm (Wan and Depew 1996; Kónyaand Scaiano 1996).

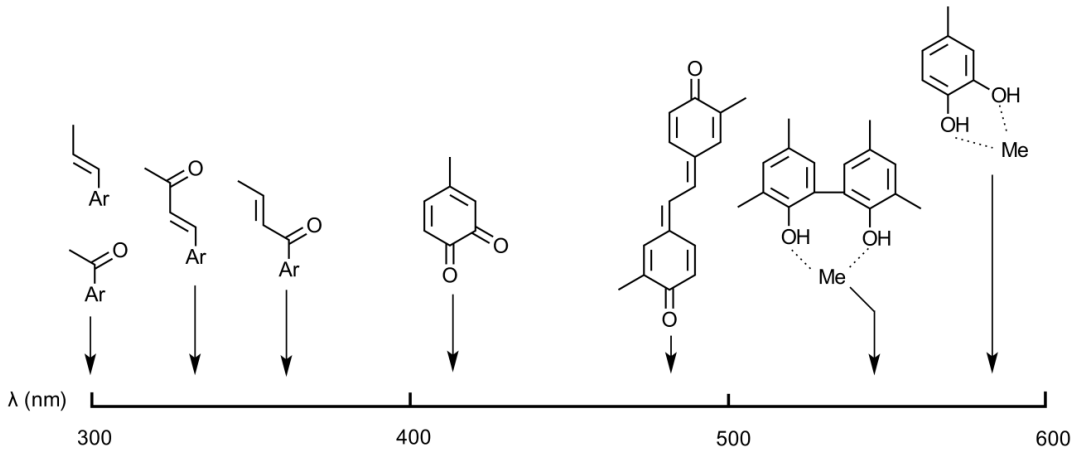

Fig. 3. Lignin-related chromophores in lignin-rich pulps and their approximate absorption maxima wavelengths (based on Gratzl 1985)

In this context, it is worth mentioning that the wavelength distribution of the energy source is of great importance relative to which groups can absorb energy and the outcome of the reactions, since it is the wavelength that determines the energy of the photons emitted. Several simultaneous reactions occur, and there is a balance between photoyellowing caused by short wavelength radiation ($\lambda < 385$ nm) and photobleaching caused by longer wavelength radiation ($\lambda > 385$ nm). This implies that irradiation with a light source that has a wavelength distribution simulating the actual aging case (window-filtered sunlight or indoor fluorescent light) is preferred.

Formation of Radicals as Intermediate Products

One of the early mechanistic insights regarding photoyellowing was that free phenolic groups are involved (Leary 1968a). Possible reactions of the free phenolic groups are shown in Fig. 4. Note that the aromatic nuclei are drawn as guaiacyl units, *i.e.*, the predominating type in softwood lignin, in all figures below. This is to simplify the presentation and does not exclude other nuclei present in wood or non-wood lignin. The hydrogen atom in a free phenolic group can be abstracted by singlet (excited) oxygen (Matsuura *et al*. 1972; Brunow and Sivonen 1975), oxygen-based radicals such as the hydroxyl and hydroperoxyl radicals (Gratzl 1985), or an excited carbonyl group (Kringstad and Lin 1970; Brunow and Eriksson 1971; Gellerstedt and Pettersson 1977). Singlet oxygen can be formed by oxygen quenching of photo-excited carbonyl groups as suggested by Brunow and Sivonen (1975) or photo-excited triplet ring-conjugated ethylenic structures (Gellerstedt and Pettersson 1975).

Singlet oxygen could, in theory, be important as an energy mediator with higher mobility than excited groups in lignin that are restricted in their movement by the solid matrix. If mediated by singlet oxygen, the excited carbonyl and phenolic groups do not need to get in direct contact for the reaction to take place (Fischer *et al*. 1995). The importance of singlet oxygen for photoyellowing and photodegradation of lignin and lignin model compounds has been put forward in several publications (Barclay *et al*. 1998, 2003; Bonini *et al*. 1998; Crestini and D'Auria 1996, 1997).

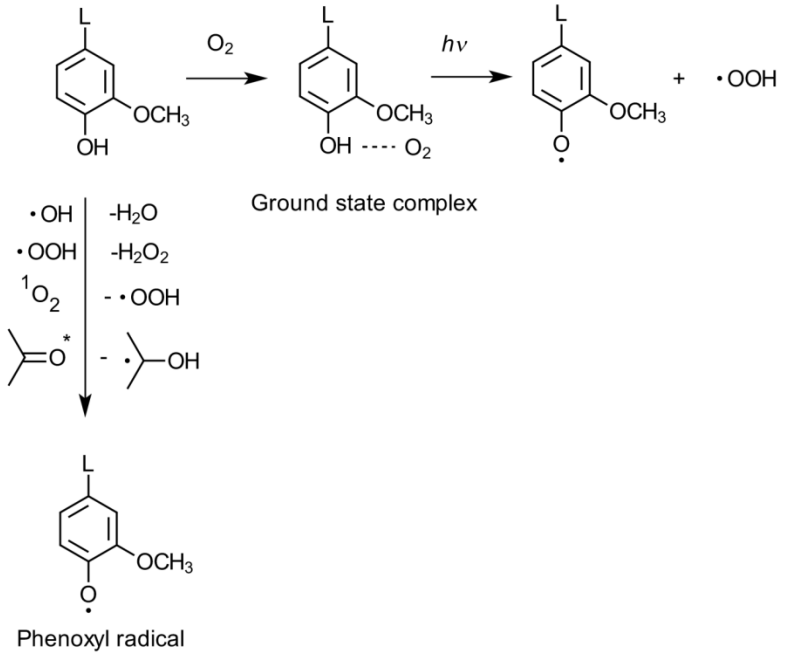

Fig. 4. Possible reactions involving the free phenolic group in lignin during light-induced yellowing (the free phenolic path). L is a connection to lignin. Main references: Kringstad and Lin 1970; Brunow and Eriksson 1971; Matsuura *et al*. 1972; Brunow and Sivonen 1975; Gellerstedt and Pettersson 1977; Gratzl 1985

It has been reported that hydroxyl radicals form during irradiation of mechanical pulp sheets (Agnemo *et al*. 1991), although others have claimed that the formation of hydroxyl radicals during irradiation is minor (Beyer *et al*. 1995). Direct photolysis of phenols in structures absorbing UV/VIS radiation in the region above 300 nm has also been researched (Kringstad and Lin 1970; Fornier de Violet *et al*. 1989; Castellan *et al*. 1990a; Jaeger *et al*. 1993). The reactions summarized in Fig. 4 can be called the free phenolic path. This pathway leads to phenoxyl radicals either by phenolic hydrogen atom abstraction by radicals or excited structures or alternatively by direct photolysis when permitted by the UV/VIS absorption characteristics of the substrate.

Figure 5 is a scheme showing the photoreactions of carbonyl groups exemplified by an α-carbonyl group. A carbonyl group can, when excited, be quenched by oxygen (giving singlet oxygen and the ground-state carbonyl), undergo C_α-C_β cleavage (Norrish Type I), or abstract a hydrogen atom, resulting in a ketyl radical. The carbonyl group can act as a photocatalyst since the ketyl radical, formed by hydrogen atom abstraction, can react with oxygen (or hydroxyl radicals, Francis *et al*. 1991) to regenerate the carbonyl group. However, the ketyl radical might also abstract another hydrogen atom (photo-reduction of the carbonyl group). Excited aryl alkyl ketones might undergo Norrish Type I cleavage, initially leading to an acyl radical and an alkyl radical. The importance of this reaction depends on the conditions (presence or absence of hydrogen donors) and the substitution pattern of the ketone. In the case of α-carbonyls, this would eventually lead to formation of end-groups of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid types. Structures of both types are common photoproducts from lignin model compounds and substrates like mechanical pulps (Hemmingson and Wong 1989; Sjöholm *et al*. 1992; Pan *et al*. 1992, 1993, 1994; Argyropoulos and Sun 1996). Note that these latter types of photoproducts can be formed from other structures as well (see below).

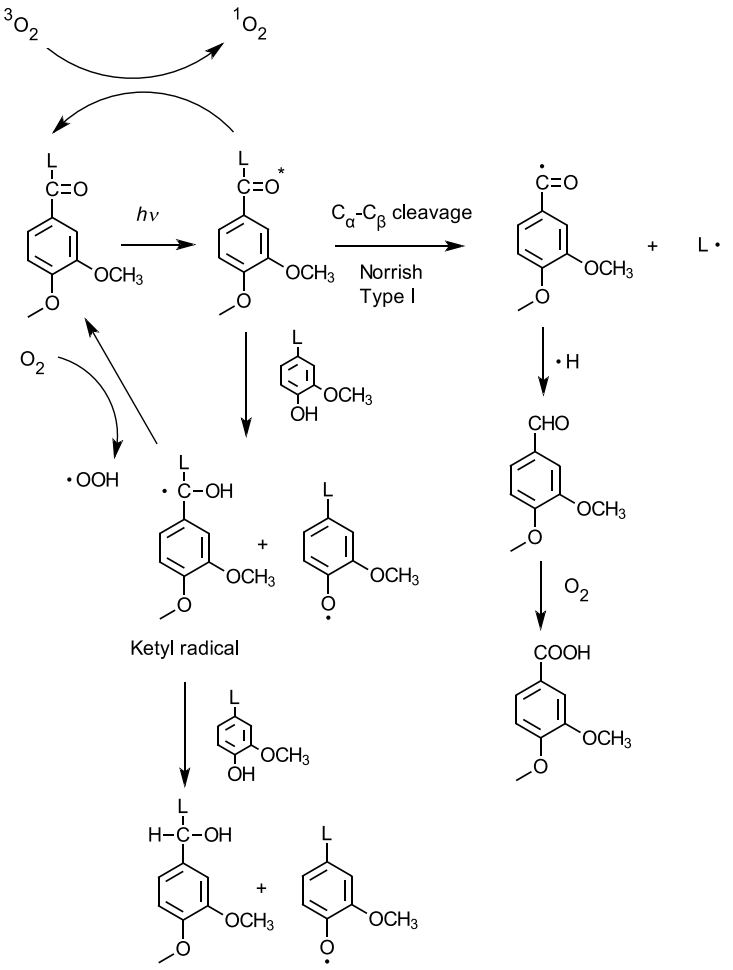

Fig. 5. Basic photoreactions of carbonyls exemplified by an α-carbonyl group. L is a connection to lignin. Main references: Kringstad and Lin 1970; Brunow and Eriksson 1971; Brunow and Sivonen 1975;Gellerstedt and Pettersson 1977; Francis *et al*. 1991

A special type of carbonyl group in lignin is the group in phenacyl aryl ethers (2-aryloxy-1-arylpropanones), made of lignin units with side-chains carrying both an α-carbonyl group and a β-O-4 linkage. Phenacyl aryl ethers have been widely studied as lignin model compounds irradiated both in solution and in solid state (Gierer and Lin 1972; Vanucci *et al*. 1988; Castellan *et al*. 1989; Netto-Ferreira *et al*. 1990; Schmidt *et al*. 1991; Fukagawa and Ishizu 1991; Hon 1992; Argyropoulos and Sun 1996; Parkås *et al*. 2004a; Lanzalunga and Bietti 2000). This type of structure can, when excited, undergo homolytic β-ether bond cleavage forming a phenacyl-phenoxyl radical pair (Fig. 6), in addition to the reactions pictured in Fig. 5. This is known as the phenacyl aryl ether pathway.

Hydrogen abstraction by the initially formed phenacyl radical leads to formation of a ketone that might further act as a sensitizer or undergo C_α-C_β cleavage. The initially formed radical pair can recombine forming the original β-O-4 linkage or another type of inter-unit bond (β-5). These types of rearrangement reactions have been shown to occur in lignin model compounds irradiated both in solution and in solid state (Fukagawa and Ishizu 1991; Argyropoulos and Sun 1996; Parkås *et al*. 2004a).

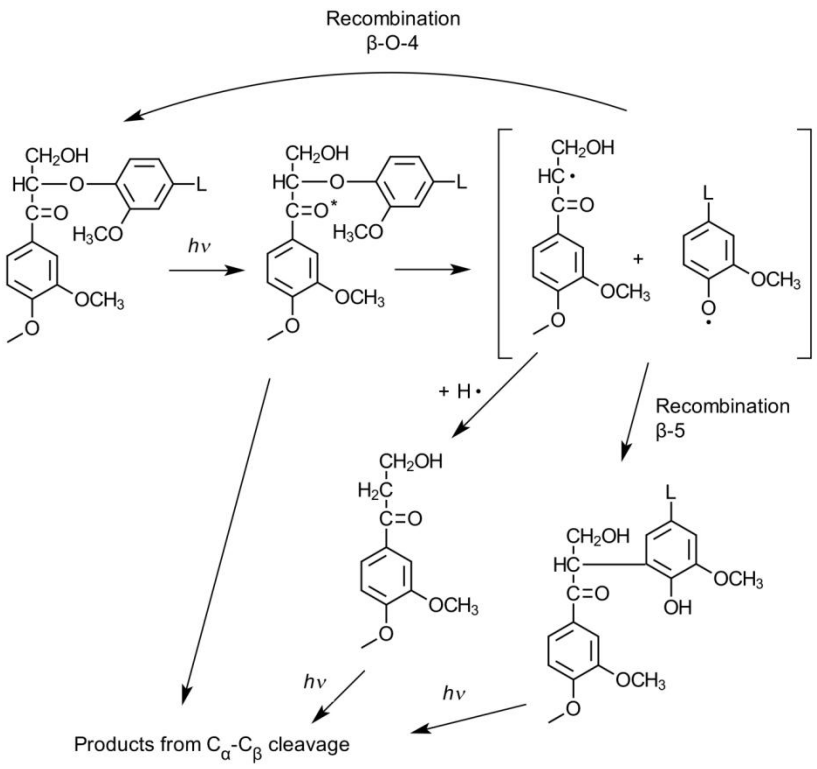

Fig. 6. Reactions of the phenacyl aryl ether units (2-aryloxy-1-aryl-propanones). L is a connection to lignin. Main references: Gierer and Lin 1972; Vanucci *et al*. 1988; Castellan *et al*. 1989; Netto-Ferreira *et al*. 1990; Schmidt *et al*. 1991; Fukagawa and Ishizu 1991; Hon 1992; Argyropoulos and Sun 1996; Parkås *et al*. 2004a

Phenacyl aryl ether cleavage can potentially result in a depolymerization of the lignin and the formation of new phenolic groups. Depolymerization (decrease in average molecular weight) of milled wood lignin isolated from softwood mechanical pulp upon irradiation in the presence of oxygen has been reported (Koch *et al*. 1994; Destiné *et al*. 1996; Wang *et al*. 1998). The depolymerisation reaction is, however, to some extent counteracted by condensation reactions due to recombination of the initial radicals, forming new β-5 linkages (Fig. 6). This explains, at least partly, the increase in C-5 condensed phenolic groups observed during irradiation of lignin in the solid state (Argyropoulos and Sun 1996; Li and Ragauskas 1999). Note that in hardwood lignin, a considerable amount of aromatic rings are of the syringyl type, that is, with a methoxyl group in position 5. This, of course, affects the possibility to form β-5 linkages. Due to the low amount of these phenacyl aryl ether structures in lignin, less than 2% of the phenylpropane units in spruce and typical hardwood milled wood lignins (Lundquist 1992; Zhang and Gellerstedt 1999; Brunow and Lundquist 2010), a major depolymerization of lignin during irradiation can hardly be explained by the cleavage of the original phenacyl aryl ether bonds in lignin, even though the content of these groups might increase during refining. A suggested alternative to the direct homolysis from the excited state in Fig. 6 is that the cleavage of the β-O-4 bond is from the ketyl radical formed after hydrogen atom abstraction of the triplet excited state carbonyl group (Scaiano *et al*. 1991, 1994). Two phenacyl radicals can, if in contact, form dimers. However in the restricted environment of mechanical pulp with a low content of phenacyl aryl ethers, this is not

likely to happen. The recombination of initially-formed phenacyl and phenoxyl radicals is, however, more likely due to their close proximity. An excited triplet state ring-conjugated carbonyl of this type could also react according to the so-called Norrish Type I reaction, leading to C_α-C_β bond cleavage and resulting in the formation of benzaldehyde structures (for example, vanillin and syringaldehyde end-groups). The substituent pattern of the ketone is of importance for reactivity, and the Norrish Type I cleavage of the phenacyl aryl ethers might be slowed down by β-phenyl quenching. The formation of these types of photoproducts has, however, been determined upon irradiation of lignin model compounds of the α-carbonyl β-ether type in solid state (Argyropoulos and Sun 1996; Parkås *et al*. 2004a). Lignin models of the α-carbonylic β-1 lignin type (deoxy-veratroin) have been shown to partly react according to Norrish Type I cleavage (Castellan *et al*. 1990b).

Another proposed reaction scheme for formation of phenoxyl radicals and depolymerisation of lignin through β-O-4 bond cleavage is the ketyl radical pathway (Schmidt and Heitner 1993b), shown in Fig. 7.

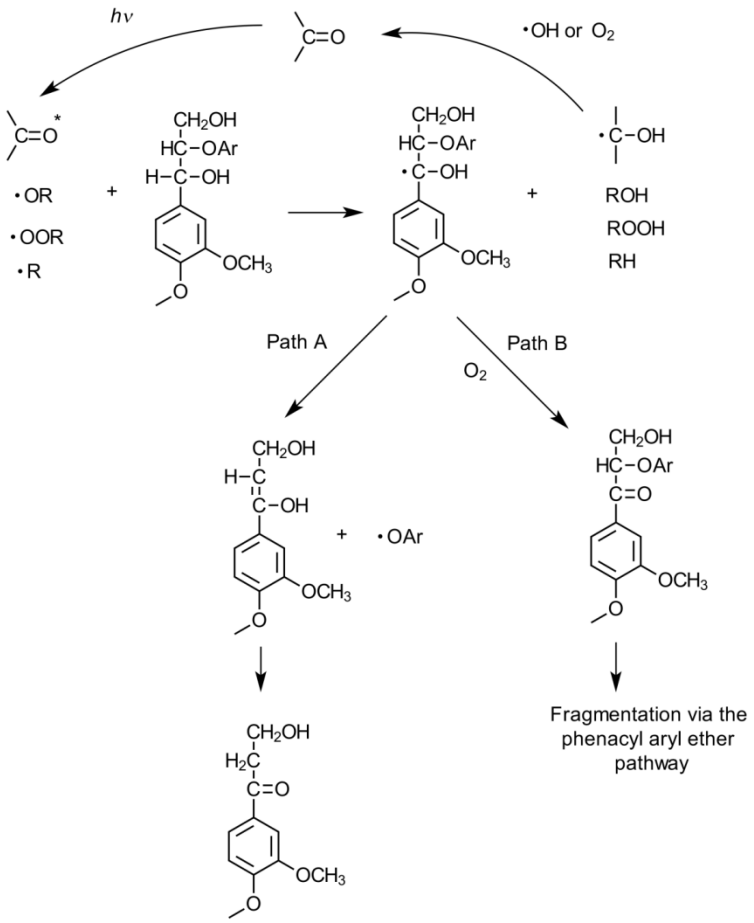

Fig. 7. Formation of ketyl radicals in lignin during photoyellowing and the further reactions either by direct ether cleavage of the ketyl radical (Path A, Scaiano *et al*. 1991; Schmidt and Heitner 1993b) or by oxygen quenching of the ketyl radical (Path B, Huang *et al*. 1995; Andersen and Wayner 1999; Fabbri *et al*. 2005). Ar is an aromatic unit.

This pathway involves the most common type of inter-unit bond in lignins, *i.e.*, the arylglycerol β-aryl ether bond. This inter-unit bond represents around 35% of the side-chains in softwood lignin and 45% of the side-chains in a typical hardwood lignin (Brunow and Lundquist 2010). Cleavage of these ether bonds might thus explain a large degradation in molecular weight as opposed to bond cleavage of the original phenacyl ether bonds. Oxygen- and carbon-centered radicals formed during irradiation are thought to abstract the hydrogen atom from the benzylic group, leading to a β-ether ketyl radical (Fig. 7). It was originally thought that the ketyl radical quickly undergoes β-ether cleavage, resulting in the formation of a phenoxyl radical and an enol (Path A) that, in turn, quickly tautomerizes to the corresponding ketone (Scaiano *et al*. 1991; Schmidt and Heitner 1993b). However, this mechanism has been challenged (Huang *et al*. 1995; Andersen and Wayner 1999; Fabbri *et al*. 2005) based on later experiments that instead indicate that the primary photoproduct from the ketyl radical is the α-carbonylic compound formed by oxygen quenching (Path B) and that the ketone and the phenoxyl radical are secondary photoproducts formed according to the phenacyl aryl ether pathway (Fig. 6 and 7).

The newly formed ketone can, of course, act as a photosensitizer, leading to further reactions. An excited carbonyl group might also abstract a hydrogen atom from a benzylic carbon, leading to a pair of ketyl radicals, both of which could form carbonyl groups under the action of oxygen or hydroxyl radicals (Francis *et al*. 1991) or photoreduce by abstracting additional hydrogen atoms. Direct photooxidation of secondary alcohols to ketones, although slow, could be quite important due to the ability of carbonyl groups to catalyze photoyellowing (Balsells and Frasca 1982; Omori *et al*. 1991) and the low amount of carbonyl groups needed to initiate the reactions. All in all, recent data presented in the literature suggests that the phenacyl aryl ether pathway might be of more importance than previously thought.

Formation of Chromophores

So far, the reactions detailed above have resulted in formation of phenoxyl radicals and, to some extent, perhaps depolymerisation of the lignin macromolecule. To display the yellow color associated with photoreversion, the initially formed structures need to form chromophores absorbing visible light in the blue-green region. It was suggested early on that these colored photoproducts might be quinones, quinone methides, and cyclohexadienones formed from intermediate phenoxyl radicals (Leary 1968a, b). The formation of *o*-quinones was suggested based on the observation that the methoxyl group content decreased during irradiation (Leary 1968a, b). Then, the formation of both *o*- and *p*-quinones from phenoxyl radicals was suggested by Lin and Kringstad (1971), based on the product pattern determined after irradiating lignin model compounds in the presence of oxygen. Their suggested mechanisms are shown in Fig. 8. Quinones are formed under the action of oxygen (and/or oxygen-centred radicals) and the different resonance forms of the stabilized phenoxyl radical. For formation of *o*-quinones, either oxygen or a hydroxyl radical reacts in position three of the aromatic ring, followed by a loss of the methoxyl group. The *p*-quinone product could be formed after a reaction in position one in the aromatic ring, resulting in side-chain displacement (Fig. 8). Quinones are present in wood lignins in amounts that are typically less than 2% of the lignin units (Brunow and Lundquist 2010). Mislankar *et al.* (1997) showed, using confocal laser scanning microscopy, that both black spruce and jack pine wood contained *o*-quinones. The highest concentrations were in the torus, middle lamella, cell corners,

and ray cells. Even after treating thin wood shavings with alkaline hydrogen peroxide, *o*-quinones were detected, despite the fact that quinones are susceptible to oxidation by alkaline hydrogen peroxide (Gellerstedt *et al*. 1980; Zhang and Gellerstedt 1999). By using solid state ^{31}P NMR spectroscopy, Lebo *et al*. (1990) could quantify the *o*-quinone content in white spruce refiner mechanical pulp before (5-6 quinone units/100 C_9-units) and after irradiation (10/100 C_9-units). This surprisingly high absolute value for quinones in refiner mechanical pulps was later proposed by Argyropoulos and Heitner (1994) to be caused by the presence of non-ionized carboxylic groups in the samples that Lebo *et al*. (1990) had not accounted for. Later studies showed that the content of *o*-quinones was only 0.7/100 C_9-units in black spruce refiner mechanical pulp (Argyropoulos and Heitner 1994) and 0.4/100 C_9-units in black spruce MWL (Argyropoulos and Zhang 1998). An increase in the *o*-quinone content during irradiation of unbleached and hydrogen peroxide-bleached SGW pulp and isolated spruce MWL has been shown in several investigations using ^{31}P NMR spectroscopy (Argyropoulos *et al*. 1995; Zhang and Gellerstedt 1999). It was also observed with fluorescence spectroscopy on hydrogen peroxide-bleached and irradiated mechanical pulp (Zhu *et al*. 1995).

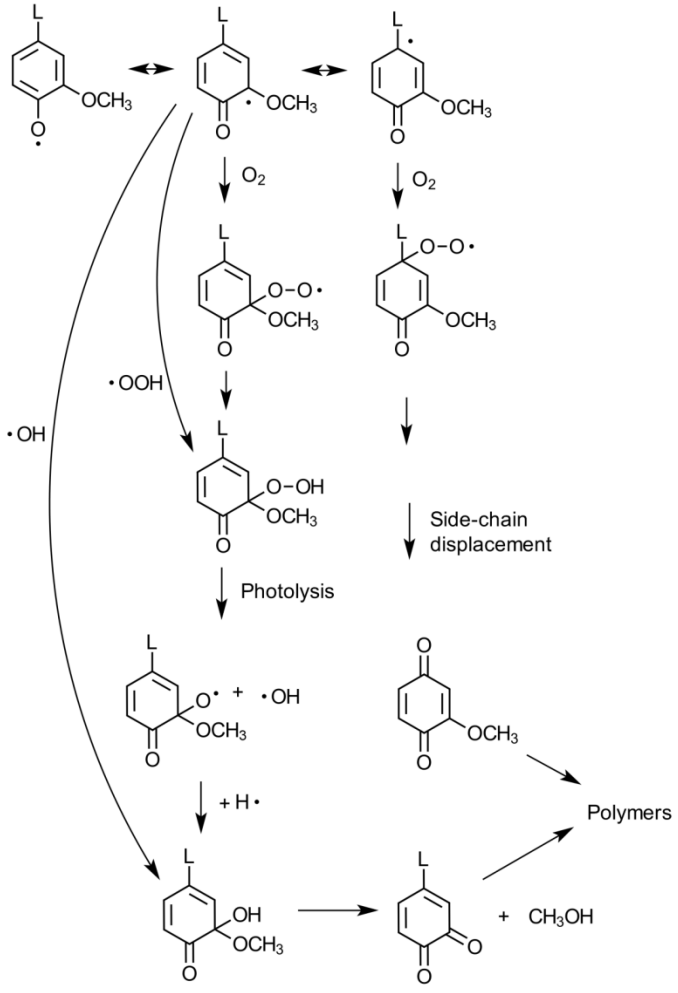

Fig. 8. Formation of *o*- and *p*-quinones from initially formed phenoxyl radicals (Lin, Kringstad 1971)

The rapid formation of *o*-quinones in the early phase of irradiation is followed by reactions leading to colored but non-quinonoid structures, based on the fact that the *o*-quinone content seems to go through a maximum (Argyropoulos *et al*. 1995; Argyropoulos and Sun 1996). The generation of *p*-quinones during photoyellowing has also been suggested to contribute to the formed color (Gellerstedt and Pettersson 1977; Forsskåhl *et al*. 1991; Hirashima and Sumimoto 1994; Jääskeläinen *et al*. 2006). Based on FT-Raman and FT-IR spectroscopic analyses of yellowed spruce thermomechnical pulp, Agarwal (1998) found support for a mechanism based on the *p*-hydroquinone/*p*-quinone redox couple as one of the major leucochromophoric/chromophoric systems (Hirashima and Sumimoto 1994). Forsskåhl and Janson (1991) reported that two bands in the UV/VIS difference reflectance spectra of bleached mechanical pulp before and after irradiation were interrelated. Irradiation in the band at 370 nm gave a response at 430 nm and vice versa, a behaviour that was either ascribed to a hydroquinone/quinone system, charge transfer complexes, quinone methides, or *E*/*Z* isomerisation of ring-conjugated double bonds (Forsskåhl and Janson 1991; Ek *et al*. 1992; Castellan *et al*. 1993a; Agarwal 1998). Agarwal and Atalla (1990) suggested that *cis*-ferulic acid is a chromophore formed during photoyellowing of white spruce mechanical pulp. To summarize, quinoid groups have been shown to form during light-induced yellowing, but they are also in themselves photoactive and could, apart from giving color, catalyze other photoreactions or react to form chromophores of both quinoid and non-quinoid types (Gierer and Lin 1972; Neumann and Machado 1989; Ek 1992; Ragauskas 1993a; Forsskåhl *et al*. 1993; Castellan *et al*. 1993b; Lennholm *et al*. 1994).

Other Reactions

In this section, reactions of cinnamaldehyde and cinnamyl alcohol end-groups will be discussed with reactions involving miscellaneous structures. The content of cinnamaldehyde units in spruce-milled wood lignin is around 4 per 100 C_9-units (one phenolic and three etherified). Approximately the same amount is found in unbleached softwood groundwood pulp (Adler and Marton 1959; Marton *et al*. 1961; Hirashima and Sumimoto 1987; Brunow and Lundquist 2010). Cinnamaldehydes are efficiently sulfonated by sodium sulphite (CTMP-production) and are degraded during alkaline hydrogen peroxide-bleaching although, in industrial practice, probably not completely (Gellerstedt *et al*. 1977; Hirashima and Sumimoto 1987; Suckling 1991; Gellerstedt and Zhang 1992; Lundquist *et al*. 2007). Cinnamyl alcohol groups are present in lignins (hardwood and softwood) in amounts of about 2% of the side-chains (Brunow and Lundquist 2010). These groups seem to be stable during refining and bleaching of mechanical pulp. The fate of the unsaturated end-groups during irradiation was studied by Gellerstedt and Pettersson (1975) by irradiating solutions of the methyl ethers of coniferyl alcohol, isoeugenol, and coniferaldehyde. The product pattern led to the suggested mechanism shown in Fig. 9. Singlet oxygen reacts with the double bond, initially giving a peroxiran, which, after rearrangement to a dioxetane, gives an aldehydic structure (*p*-hydroxybenzaldehyde type end-group) that in turn can oxidize to the corresponding carboxylic group. Gellerstedt and Pettersson (1975) found the methyl ether of coniferaldehyde to be stable during irradiation both in solution and solid state. Hirashima and Sumimoto (1987) also found that filter paper impregnated with coniferaldehyde (and its methyl ether) in amounts corresponding to the levels found in untreated groundwood pulp did not show a brightness loss when irradiated. This indicates that the photoproducts from this type of end-group do not contribute significantly to the

total color change upon irradiation of mechanical pulps, but as a photo-initiator, it could be more important due to the clear absorption of UV/VIS by cinnamaldehydes. On the other hand, the methyl ethers of coniferaldehyde and coniferyl alcohol deposited on filter paper both gave decreased brightness when irradiated, and in both cases veratraldehyde and veratric acid were formed as photoproducts together with oligomeric/polymeric material (Castellan *et al*. 1991; Omori *et al*. 1992; Parkås *et al*. 2004a). These oligomerizations are not likely in a true ageing case with few end-groups in direct contact. However, indications that model compounds of this type react with the cellulosic substrate might be important (Jaeger *et al*. 1993).

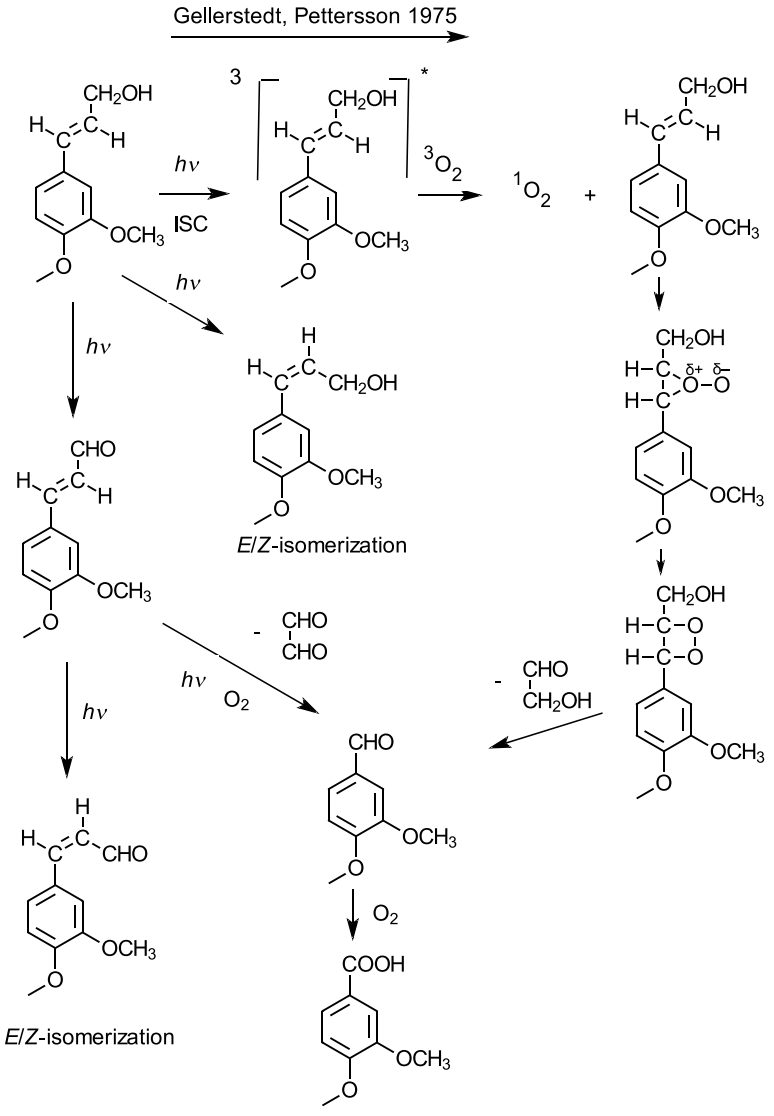

Fig. 9. Reactions of cinnamaldehyde and cinnamyl alcohol end-groups exemplified by their guaiacyl analogue. Main references: Gellerstedt and Pettersson 1975; Castellan *et al*. 1991; Omori *et al*. 1992; Pan *et al*. 1992; Parkås *et al*. 2004a,b,c)

Other reactions that can occur during irradiation of cinnamyl alcohol structures, as shown by etherified model compound studies in solid state are: oxidation of cinnamyl alcohol to cinnamaldehyde and *E*/*Z*-isomerization of both cinnamaldehydes and cinnamyl alcohols (Parkås *et al*. 2004a). Oxidation of cinnamyl alcohol groups to cinnamaldehydes

could explain the increased amounts of cinnamaldehydes found after irradiation of bleached spruce TMP (Pan *et al*. 1992) or ^{13}C-labelled dehydrogenation polymers in solid state (Parkås *et al*. 2004b, c). The different results regarding the behaviour of cinnamaldehydes during photoageing might also be due to the different irradiation sources used in the various investigations.

Some important leucochromophores that might be formed during refining and bleaching of mechanical pulps have been briefly mentioned above. Examples of these are stilbenes formed from β-5 and β-1 structures in lignin during refining and hydrogen peroxide bleaching, phenylcoumarones formed from β-5 units, and stilbene *para*-hydroquinones from stilbenes via the Dakin reaction during alkaline hydrogen peroxide bleaching. The formation and photoreactions of these structures are outlined in Fig. 10. Side chains attached to phenolic units, either by a conjugated double-bond or an α-carbonylic group, can, during bleaching with alkaline hydrogen peroxide, form hydroquinones by side chain displacement (Gellerstedt and Agnemo 1980b). This process is shown in Fig. 10a. Hydroquinones are, in general, easily oxidized to corresponding *p*-quinones (Castellan *et al*. 1993a). This rapid oxidation of leucochromophoric hydroquinones (or catechols) to *p*-quinones and *o*-quinones might help explain the initial fast brightness loss seen during irradiation and could also explain the higher sensitivity of hydrogen peroxide-bleached mechanical pulps to photoyellowing when compared to unbleached pulps. Gellerstedt and Zhang (1992) concluded that diguaiacyl stilbenes, mainly from β-1 units, were the leucochromophores responsible for the fast initial photoyellowing of hydrogen peroxide-bleached pulps (Fig. 10b) based on mild hydrolysis of spruce wood and several unbleached, hydrogen peroxide-bleached, and irradiated spruce mechanical pulps and the subsequent identification of released lignin-derived monomers, dimers, and some trimers. Based on this, a model compound trial was performed with two monophenolic diguaiacyl stilbenes irradiated in solid state, deposited on filter paper (Zhang and Gellerstedt 1994b). The only colored structure identified was the corresponding stilbene ortho-quinone. Apart from the quinone, products from cyclodimerization [2π+2π] of excited and ground-state stilbenes in the form of tetraphenylcyclobutanes were found. Although theoretically interesting, the relative scarcity of the stilbenes in pulp lignin makes this reaction less important from a practical ageing perspective. Since excited stilbenes also can undergo cycloaddition with other ethylenic structures (*e.g*. cinnamyl alcohols or cinnamaldehydes), similar reactions might have some importance. However, they do not primarily lead to the formation of color. Fast color formation upon irradiation of stilbene model compounds was also reported by Weir *et al*. (1995b). On the other hand, Ruffin *et al*. (1998) concluded that the *para*-stilbene phenols formed from β-1 structures are scarce in hydrogen peroxide-bleached pulp and that they could not explain the rapid yellowing of bleached mechanical pulps. After refining and hydrogen peroxide bleaching, β-5 structures might form leucochromophoric groups of stilbene hydroquinone type (Lee and Sumimoto 1991, Fig. 10c). Model compound studies in solid state have shown that the highly colored corresponding quinone is formed rapidly upon irradiation (Ruffin and Castellan 2000). In solution state, additional reactions leading to phenanthrene quinone by photocyclization of the *Z*-stilbene hydroquinone were found. The photochemistry of phenolic and methylated lignin models of the phenylcoumarone type have been studied by Noutary *et al*. (1995a, b). Both models were photoactive, the phenolic more than the etherified, forming colored coupling products as well as phenylcoumarone *o*-quinone. This demethylation reaction is possible, whereas a coupling between two phenylcoumarones is very unlikely to occur in

pulp. The frequency of β-1 structures is higher in hardwood lignin than in softwood lignin, while the occurrence of β-5 (phenylcoumaranes) is higher in softwood than hardwood lignin (Brunow and Lundquist 2010).

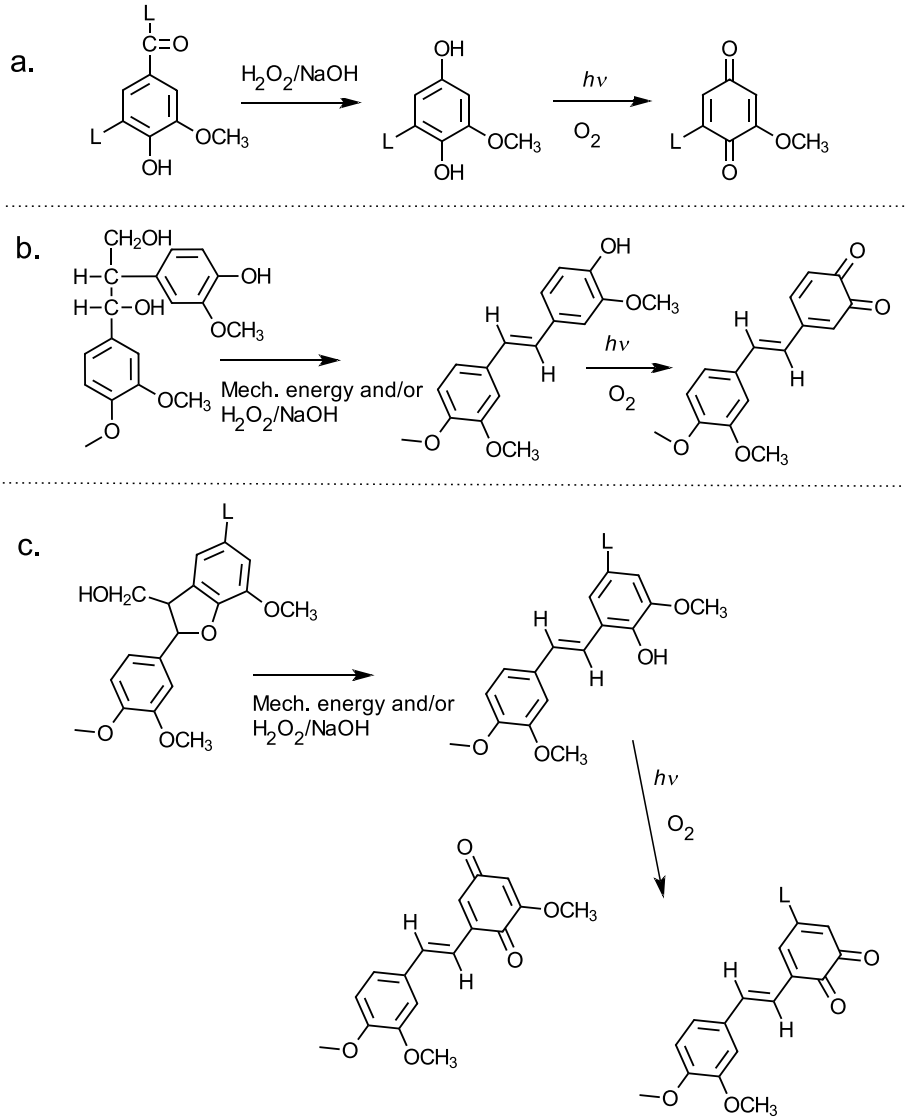

Fig. 10. Formation of hydroquinones, stilbenes, and quinones during refining, hydrogen peroxide bleaching, and irradiation of mechanical pulp. Main references: Gellerstedt and Agnemo 1980b; Lee and Sumimoto 1991; Gellerstedt and Zhang 1992; Castellan *et al*. 1993a; Zhang and Gellerstedt 1994b; Ruffin and Castellan 2000)

The discovery of the dibenzodioxocin structure in lignin (Karhunen *et al*. 1995) has not passed unnoticed in the field of photoyellowing. Even though the mechano-chemical reactions and the reactions during alkaline peroxide bleaching of this structure are poorly known, model compounds of this type have been irradiated in solution and studied (Gardrat *et al*. 2004, 2005; da Hora Machado *et al*. 2006). An etherified dibenzodioxocin model in benzene reacted during irradiation through homolytic cleavage of both α-O-4 and β-O-4 bonds, implying a potential mechanism for lignin depolymerization at a branching point in lignin (Fig. 11).

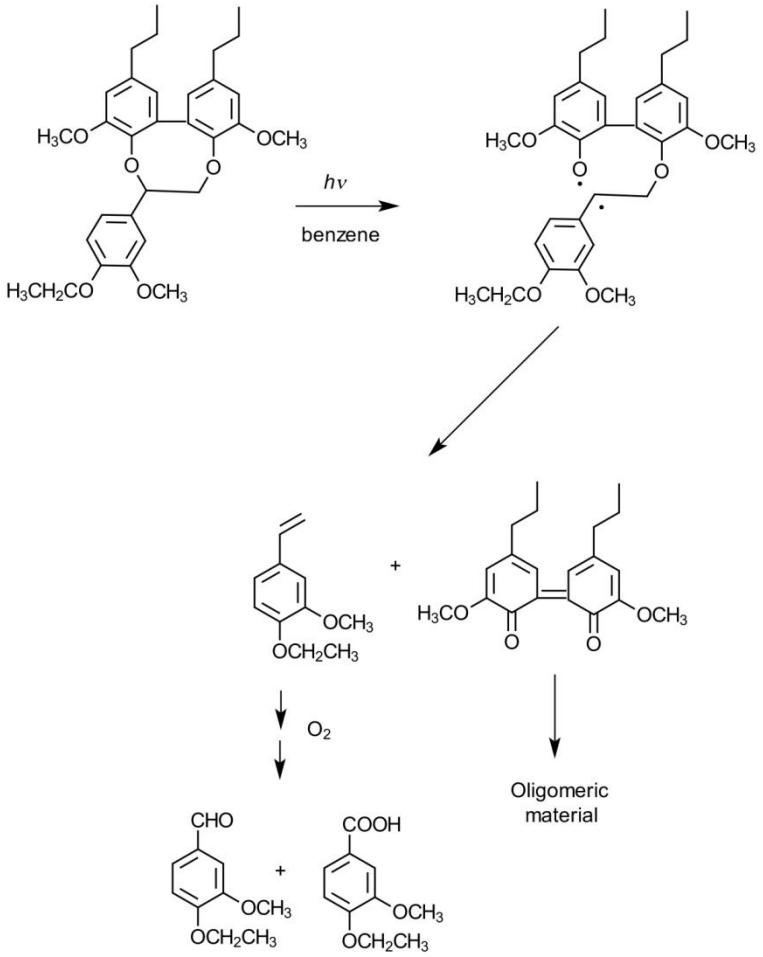

Fig. 11. Photochemistry of an etherified lignin model compound of the dibenzodioxocin type irradiated in solution (benzene). Adapted from Gardrat *et al*. (2004)

The formation of colored materials such as 2,2'-diphenoquinone and oligomeric colored material was suggested (Gardrat *et al*. 2004). Irradiation of the corresponding phenolic lignin model compound in ethanol resulted in lower degradation efficiency (lower quantum yield), possibly due to the reversible formation of the quinone methide (Gardrat *et al*. 2005). In recent years, analytical techniques designed to capture radicals and analyze stable products by ^{31}P NMR spectroscopy and gas chromatography-mass spectrometry have been further developed (Argyropoulos *et al*. 2006; Zoia and Argyropoulos 2009, 2010). More experiments using this technique in the study of light-induced yellowing might reveal further important knowledge regarding the mechanism of discoloration.

PHOTOSTABILIZING METHODS FOR LIGHT-INDUCED YELLOWING

A large number of photostabilizing treatments to protect lignin-rich pulps against ultraviolet and visible radiation have been proposed and evaluated during the last seventy years. The treatments can be divided into three main categories (Fig. 12). The first is

characterized by hindering ultraviolet radiation from reaching the photosensible structures in lignin, which can be done by adding UV-absorbing compounds or by coating the paper. The second category includes treatments that function by suppressing the formation of chromophores by chemical modification of functional groups in the lignin moiety that can absorb UV radiation or that can generate reactive intermediates (*e.g.* phenoxyl and ketyl radicals). The last category is characterized by disrupting the color forming reactions by addition of inhibitors, such as quenchers, which inactivate excited molecules and/or antioxidants, which trap intermediate radicals.

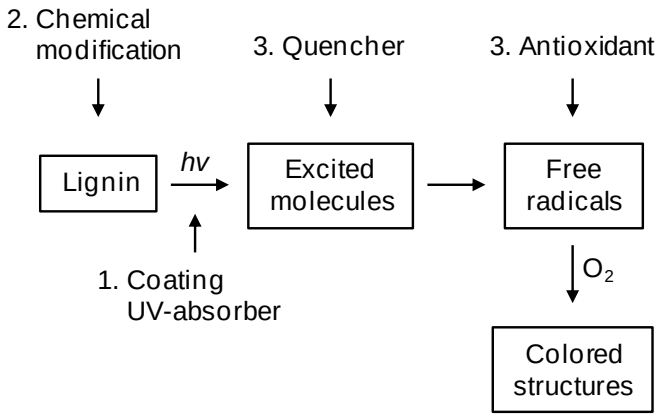

Fig. 12. Schematic description of the different proposed inhibition methods for light-induced yellowing of lignocellulosic materials

The extent of photostabilization needed is dependent on the lifetime expectancies of the lignocellulosic product, on the conditions under which the product is used, and on the amount of high-yield pulp (*i.e.* amount of lignin) used in the product. The UV/VIS radiation, temperature, and humidity conditions may vary considerably between different end-use applications and geographical locations, and the extent of stabilization needed will thus also vary. It is, however, a prerequisite that a photostabilizing treatment is environmentally, technically, and economically feasible to be considered an option. Even though there are possibilities to more or less completely retard the light-induced discoloration, no treatment that can inhibit photoyellowing of a product composed of a substantial amount of high-yield pulp and can fulfill all of the demands above exists today. An overview of the proposed photostabilizing treatments, divided according to the categories in Fig. 12, is given below. Special attention will be focused on the photostabilization characteristics of products, where a part of the fiber content is of high-yield origin, since this is the highest potential for growth of mechanical and chemimechanical pulps in long-life paper and board products.

Absorption or Scattering of Ultraviolet Radiation

One obvious way of improving the photostability is to protect the lignin against exposure to ultraviolet radiation, *i.e.*, to prevent the radiation from reaching the chromophores. This can be done by introducing an ultraviolet absorbing compound on the paper surface or in the paper itself, in order to introduce a compound that converts the absorbed radiation to non-harmful thermal energy. It is also possible that UV absorbers may function as antioxidants, as triplet quenchers, or via photoionization (Castellan *et al*. 1994; Weir and Miller 2000). Efficient UV screens are hydroxybenzophenone and

benzotriazole derivatives (Kringstad 1969, 1973; Gellerstedt *et al*. 1983; Fornier de Violet *et al*. 1990; Li and Ragauskas 2000; Li *et al*. 2004). The performance of 2,4-dihydroxybenzophenone has been improved by the introduction of cationic groups, which facilitate the location of the benzophenone derivative to lignin-rich areas of the fiber material (Castellan *et al*. 1994). Novel water-soluble hydroxybenzophenones containing ionic or neutral amino groups have been synthesized and proven to be efficient photostabilizers (Argyropoulos *et al*. 2000). A favorable synergistic effect between hydroxybenzophenone or hydroxyphenylbenzotriazole type ultraviolet absorbers and thiols or sodium hypophosphite has been reported (Davidson *et al*. 1995; Trichet *et al*. 1996) and ascribed to the regeneration of the UV absorber by reduction (Noutary *et al*. 1994, Gugumus 1993), whereas others have reported that the improved stability is not due to a regeneration mechanism (Cook and Ragauskas 1997). A combination of a UV screen (benzotriazole derivative), polyethylene oxide dithiol, and high charge of sucrose has also been used to photostabilize different types of high-yield pulps with some success (Petit-Conil *et al*. 1998). Another effective additive combination that has been explored for stabilizing hardwood and softwood pulps is the system 2,4-dihydroxybenzophenone/ thiol/ascorbic acid (Pan *et al*. 1996). The addition of a UV screen in combination with in situ peroxyborate bleaching has been suggested as a possible photostabilizating system for high-yield pulps (Liu and Argyropoulos 1998; Moore and Argyropoulos 2000). A dual component system that has been thoroughly examined and that efficiently inhibits yellowing of mechanical pulps is the system consisting of a benzotriazole derivative (UV absorber) and a hindered nitroxide radical scavenger (4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl) (McGarry *et al*. 2000; Beaton and Argyropoulos 2001; Yuan *et al*. 2002; 2003). The effectiveness of the system is claimed to be partly due to an increased photostability of the ultraviolet absorber in the presence of the nitroxide and partly due to inhibition of the cleavage of β-O-4-aryl ether linkages (Beaton and Argyropoulos 2001). These additives have, however, limited ability to absorb on pulp fibers and therefore need to be applied in a size press or as an additive in the coating layer. Hindered nitroxide and hydroxylamine radical scavengers with a higher affinity for mechanical pulps have been synthesized (Hu 2003b, 2004; Hu *et al*. 2005). These inhibitors may be suitable for treating the high-yield pulp separately; something that could improve the economic performance of the dual system for papers containing only part mechanical pulp since the chemical pulp fraction in the papers can be left untreated. Ultraviolet absorbers used alone or in combination with other inhibitors have the poten-tial to improve the photostability of lignin-rich pulps, but to be a realistic alternative, the efficiency/cost ratio needs to be improved.

The use of fluorescent whitening agents (FWAs) to retard photoyellowing has been reported by several researchers (*e.g*. Bourgoing *et al*. 2001; Ragauskas *et al*. 2001; Li and Ragauskas 2001; Zhang *et al*. 2009a, b). Fluorescent whitening agents are used in the pulp and paper industry to improve the optical properties and are often derivatives of diaminostilbene sulfonic acids or distyrylbiphenyl compounds that absorb radiation in the ultraviolet range (λ_{max} ~350-360 nm) and re-emit the energy within the visible blue region (λ_{max} ~440 nm), *i.e*., these compounds act as UV screens. It has been proposed that FWAs are most effective in retarding the slow phase of reversion (Ragauskas *et al*. 2001). FWAs can be added in the wet-end of the paper machine, in a size press or coating layer, or in the bleach plant. Although fluorescent whitening agents retard discoloration, relatively large amounts are needed, and the effect is only temporary. The fluorescent whitening agent is photochemically degraded, creating a loss of fluorescence over time as

a result (Bourgoing *et al*. 2001). Nevertheless, FWA is an important additive for high-brightness papers containing part high-yield pulps, and it has been reported that fluorescent whitening agents, especially in combination with fillers, significantly retard the discoloration for these products (He *et al*. 2010; Perng and Wang 2010). Different types of fillers have also been examined for their inhibiting capacity. Zinc oxide and titanium dioxide that both absorb and scatter ultraviolet radiation can significantly retard photoyellowing of hydrogen peroxide-bleached softwood TMP (Kang and Ni 2006). However, the required addition amounts are high, and these pigments are much more expensive than other fillers.

Paper and board are often coated to improve their printability and optical properties. Coatings also block the damaging ultraviolet radiation by absorbing or scattering radiation or by concealing a part of the discoloration of the base paper (Fjellström *et al*. 2007b). It is most likely necessary to coat a paper if pulps containing lignin are to be used as the main fiber component in the furnish. The coat-weight will affect the ability of the radiation to pass through the coating (Johnson 1989, 1991; Ghosh *et al*. 2002; Yuan *et al*. 2006; Fjellström *et al*. 2007b). The amount and type of pigment in the coating color will affect the protective capacity; titanium dioxide and zinc oxide pigments being the most effective, followed by kaolin, precipitated, and ground calcium carbonate pigments (Gellerstedt *et al*. 1983; Reinhart and Arneberg 1988; Luo and Göttsching 1991; Beyer *et al*. 2006a; Fjellström *et al*. 2009; Li *et al*. 2011). A narrow pigment size distribution is beneficial for reducing the amount of ultraviolet radiation that reaches the base paper (Fjellström *et al*. 2009; Lindblad *et al*. 1989). The binders, thickeners, and additives, including FWA and carriers for FWA, such as polyvinyl alcohol, polyethylene glycol, carboxymethylcellulose, and polyvinylpyrrolidone, may also affect the stability of the coated paper (Reinhardt and Arneberg 1988; Luo and Göttsching 1991; Fjellström *et al*. 2009). Low- and medium-weight coating layers provide only partial protection against deterioration by light, and it is necessary to add other inhibiting compounds for successful stabilization. Good results have been reported with a combination of a radical scavenger (hydroxylamine-type) and a UV absorber (benzotriazole derivative or titanium dioxide) at moderate coat weights (El-Sadi *et al*. 2002; Yuan *et al*. 2004 a, b). Even though coating a lignin-containing paper is one of the most promising stabilizing treatments, the costs associated with the ultraviolet absorbing/scattering pigments and inhibitors necessary are still too high if a substantial amount of the chemical pulp is to be replaced with a mechanical or chemimechanical pulp. A high substitution degree will negatively impact the photostability of the product and a higher coat weight or charge of additives will therefore be needed (Johnson 1989, 1991; Paulsson *et al*. 2002; Fjellström *et al*. 2007a; He *et al*. 2009).

Chemical Modification

The chemical modification approach of potential chromophoric or leucochromophoric groups in lignin involves the reduction of carbonyl groups, hydrogenation of ring-conjugated ethylenic groups, and acylation or alkylation of hydroxyl groups. Ring-conjugated carbonyl groups participate in several of the proposed reaction sequences leading to discoloration. Therefore, many attempts have been made to remove these groups by reductive treatments. Sodium borohydride reduction of spruce SGW pulp (Manchester *et al*. 1960; Leary 1968a; Ek *et al*. 1990), spruce TMP (Tschirner and Dence 1988; Francis *et al*. 1991; Schmidt and Heitner 1991; Paulsson *et al*. 1995), or softwood CTMP (Fornier de Violet *et al*. 1989; Castellan *et al*. 1992a) did not have any dramatic

effect on the overall discoloration rate, despite the fact that milled wood lignin or carbonyl-containing lignin model compounds were substantially stabilized by the chemical treatment (Lin and Kringstad 1970). Other reducing agents (dithionite, thiourea dioxide, dithionite, diboran) were also ineffective in suppressing the light-induced discoloration (Manchester *et al*. 1960; Andrews and DesRosiers 1966; Tschirner and Dence 1988). The low efficiency of reductive treatments may be due to incomplete reduction of carbonyl groups, and since only a few carbonyl groups are needed to catalyze photoyellowing reactions, care must be taken when evaluating the results from the studies. A further explanation of the ineffectiveness is the presence of other potential chromophoric structures not removable by reduction or the formation of new carbonyl groups during irradiation (see Fig. 7). A method for selective removal of α-carbonyl and α-hydroxyl groups has been proposed (Hu *et al*. 1999a), and could, according to the authors, possibly hinder ketyl radical formation during photoyellowing.

Reduction in combination with hydrogenation has been reported to be effective in stabilizing lignin model compounds and milled wood lignin towards photoinduced degradation (Lin and Kringstad 1970; Castellan *et al*. 1992b), but was ineffective in reducing the discoloration of spruce TMP (Tschirner and Dence 1988). It is possible that the discrepancy in obtained results is related to the difficulty in reducing vinylic double bonds in the fiber structure. A method for mild catalytic hydrogenation of lignin aromatics in lignin model compounds and MWL has been described (Hu *et al*. 1997a, b, 1999b) and if a catalyst that can diffuse into the fibers and catalyze the hydrogenation of pulp lignin substrate could be developed, photoyellowing might be inhibited permanently.

One of the most effective treatments tested so far has been to chemically modify hydroxyl groups in softwood or hardwood lignins through etherification or esterification reactions. A variety of alkylation and acylation modifications including acetylation, methylation, benzoylation, and hydroxyethylation have been tested. Many researchers have shown that these treatments not only increase the photostability of high-yield pulp, but often brighten and, in some cases, also photobleach the pulp. Methylation has been reported to inhibit photoyellowing (Peill 1946; Callow 1947; Andrews and DesRosiers 1966; Leary 1968a) but not to affect the rate of chromophore formation during photoyellowing (Schmidt and Heitner 1991). Acetylation with acetic anhydride was reported early on to increase the photostability of jute fibers (Peill 1946; Callow 1947, 1952), and acetylation was later found to photostabilize, and in some cases, also brighten high-yield pulps (Manchester *et al*. 1960; Leary 1968a; Lorås 1968; Ek *et al*. 1992; Paulsson *et al*. 1995; Hirashima and Sumimoto 1996; Itoh *et al*. 1997, Agarwal 1998; Paulsson and Ragauskas 1998b; Agarwal 1999). Acetylation has also been reported to increase the photostability of MWL (Agarwal *et al*. 1999; Heitner *et al*. 2001), isolated aspen and softwood bleached CTMP lignins (Pu *et al*. 2003; Pu and Ragauskas 2005), and wood (Dunningham *et al*. 1992; Plackett *et al*. 1992; Hon 1995; Ohkoshi 2002). Acetylation is thought to be a single-site reaction that is acid- or base-catalyzed. Acetic acid is formed as a byproduct during the reaction. Examples of catalysts that have been used are pyridine, zinc chloride, dimethylformamide, urea-ammonium sulfate, magnesium perchlorate, trifluoroacetic acid, boron trifluoride, sodium acetate, potassium hydrogen phosphate, potassium acetate, and γ-rays (Rowell 1982). Acetylation can, however, also be performed without any catalyst. The photostabilizing effects of acetylation are most pronounced in the initial phase of derivatization. Therefore, structures that are important for discoloration can be expected to be found among those

that react during this initial phase. Lignin model compound studies have shown that phenols, hydroquinones, and catechols were easily acetylated, although not completely (Paulsson *et al*. 1996a, b). This is in agreement with the observations that most of the free phenolic hydroxyl groups in unbleached and hydrogen peroxide-bleached, high-yield pulps are removed at a moderate extent of derivatization (Paulsson *et al*. 1995). The γ-hydroxyl groups in models of the β-O-4 type and coniferyl alcohol type are comparatively rapidly acetylated, whereas α-hydroxyl groups in β-O-4 models seem to be more resistant towards acetylation (Paulsson *et al*. 1996a, b). Later, similar results were reported for acetylated hydrogen peroxide-bleached aspen lignin; the order of reactivity was found to be phenolic OH >> γ-side chain OH > α-side chain OH (Pu and Ragauskas 2005; Haque and Hill 2000). Others have not, however, found any evidence for selective acetylation of phenolic hydroxyl groups in MWL at a low degree of derivatization (Heitner *et al*. 2001). Further, *o*-quinoidic model compounds were rapidly decomposed and to a large extent decolored on acetylation, whereas *p*-quinoidic model compounds were essentially unaffected by the chemical treatment (Paulsson *et al*. 1996b). Other alkylation and acylation agents such as ethylene oxide, propylene oxide, butylene oxide, benzoyl chloride, methyl chlorocarbonate, and propionic anhydride have also been found to be effective in photostabilizing high-yield pulps (Singh 1966; Wallis and Wearne 1982; Paulsson and Parkås 2000). Removal of phenolic hydroxyl groups via catalytic hydrogenolysis has been reported to result in a significant yellowing inhibition of lignin model compounds (Hu *et al*. 2000).

Although successful photostabilization has been achieved by derivatizing lignin hydroxyl groups in lignocellulosic materials, no treatment has yet become technically or economically feasible due to the large amounts of chemicals required for successful protection and due to the deterioration in strength and optical properties accompanying some of the treatments. Furthermore, many of the chemicals used (*e.g.* for methylation and epoxidation modifications) are highly toxic, and the use of these chemicals is therefore highly questionable.

Inhibiting Compounds

The photoyellowing process involves a series of radical reactions and free radical scavengers, which often function as proton donators and have therefore been extensively explored. Sodium citrate and sodium ascorbate were reported early on to increase the photostability of high-yield pulps (Kringstad 1969). Later, ascorbic acid was found to be an efficient stabilizer for different types of high-yield pulps (Fornier de Violet *et al*. 1990; Agnemo *et al*. 1991; Schmidt and Heitner 1991; Wan *et al*. 1993). However, the inhibition was only temporary, and the inherent thermal instability of ascorbic acid is a serious limitation for the use of this antioxidant (Ragauskas 1994; Schmidt and Heitner 1997).

Sulfur and phosphorous compounds, often used as antioxidants in polymers, have been tested as inhibitors, and examples of compounds with a photostabilizing effect are: 1-thioglycerol, dimercaptoacetate, thioglycolic acid, 2,2'-oxydiethanethiol, ethylene glycol bisthioglycolate, thiosulfinates, and 1-dodecanethiol (Cole and Sarkanen 1987; Janson and Forsskåhl 1989; Fischer 1990; Daneault *et al*. 1991; Pan and Ragauskas 1995a, b; Cook *et al*. 1996; Li *et al*. 1999; Barnett *et al*. 2002). The stabilizing effect of sulfur-containing compounds decreases over time, and the unpleasant odor is a serious problem that makes these compounds unsuitable for most applications. However, a group of novel non-odorous thiols, isolated from biomaterials or synthesized, have been found

to be effective in retarding the discoloration of aspen CTMP (Beyer *et al*. 2006b). The sulfur-containing inhibitors were found to protect the lignin-containing paper for a long time when combined with an ultraviolet absorber and as part of a coating layer.

Different types of water-soluble, colorless, and odorless phosphinates have also been proposed and tested with moderate inhibition of photoyellowing of bleached softwood CTMP (Guo and Gray 1996; Guo *et al*. 1997). Addition of radical scavengers, such as phenyl-N-*t*-butylnitrone, phthalic hydrazide, 1-hexanol, or colloidal sulfur during milling of TMP significantly reduced photoyellowing (Wu *et al*. 1994), and it was proposed that the mechanochemical conversion of lignin to photoactive structures was hindered or stopped. This has, however, not been verified in later studies where different types of antioxidant and radical scavengers were added during refining (Zhu *et al*. 1997).

Naturally occurring antioxidants, *e.g.*, quercetin, catechin, α-tocopherol, and avenanthramides, have been evaluated for their capacity to inhibit light-induced discoloration with very limited success (Fagerlund *et al*. 2003). Polymers such as polyethylene glycol, polyvinyl-pyrrolidone, and polytetrahydrofuran with different molecular weights and end groups can retard photoyellowing if relatively large amounts are used (Minemura 1978; Forsskåhl and Janson 1992; Cole *et al*. 1993; Hortling *et al*. 1993; Rättö *et al*. 1993; Davidsson *et al*. 1995; Janson and Forsskåhl 1996). The exact mechanism behind the stabilization obtained by polymers is not known.

Another class of inhibitors is quenchers, *i.e.*, molecules that can relax excited chemical structures. Naphthalene derivatives that function as α-carbonyl triplet quenchers (Fornier de Violet *et al*. 1990) and 1,4-diazabicyclo[2.2.2]octane (DABCO) that quenches singlet oxygen (Janson and Forsskåhl 1989) have shown no or very limited inhibiting effect when applied to pulp. DABCO could, however, decrease the photooxidative degradation of MWL (Wang *et al*. 1996) and suppress the formation of quinones during photolysis of lignin in solution (Neumann and Machado 1989). Hexadienol *trans*,*trans*-2,4-hexadiene-1-ol has been reported to retard yellowing as efficiently as ascorbic acid (Ragauskas 1993b; Harvey and Ragauskas 1996). The photostabilizing activities of diene-type structures are believed to be due in part to radical scavenging properties and in part by quenching the excited state of lignin (Schmidt *et al*. 1991; Pan *et al*. 1996).

Since transition metal ions present in pulp or paper aggravate discoloration, chelating agents have also been tested as inhibitors. The addition of diethylene-triaminepentaacetic acid, either by spraying (paper) or in situ (pulp), was found to reduce both the light-induced and heat-induced discoloration of maple CTMP (Ni *et al*. 1998). Others have, however, found that chelating agents photostabilize mechanical pulps only if the chelants are thoroughly washed from the fiber material prior to ageing (Janson and Forsskåhl 1989).

Although some of the proposed inhibiting compounds have the possibility to retard discoloration, relatively large amounts of the additive are needed, and they will only temporarily delay the discoloration. Synergistic effects have been reported for certain inhibitor mixtures (Davidson *et al*. 1995; Cook and Ragauskas 1997; McGarry *et al*. 2000; Ragauskas *et al*. 2001), and it is has been proposed that a successful photo-stabilization technology needs an ultraviolet absorber, an excited state quencher, and a radical scavenger (Pan *et al*. 1996). Such technologies are, with the inhibitors known today, not cost-effective.

CURRENT STATUS: PHOTOYELLOWING MECHANISMS AND PREVENTIVE METHODS

Acetylation of lignin-rich mechanical and chemimechanical pulps removes most of the free phenolic hydroxyl groups after a short reaction time, and the photostabilizing effect is most pronounced at the initial phase of acetylation (Paulsson and Simonson 2002). Model compound studies have shown that phenols, hydroquinones, catechols, and *o*-quinones are rapidly acetylated, whereas benzylic hydroxyl groups (and *p*-quinones) are more resistant to acetylation (Paulsson *et al*. 1996 a, b; and Ragauskas 2005). There is nothing to suggest that α-hydroxyl groups should be more reactive in the pulp than in the model compound studied. The number of underivatized benzylic hydroxyl groups present in the lignin moiety at an acetylation level, which to a large extent inhibits the photo-yellowing of high-yield pulps, can thus be expected to be fairly high. It is therefore difficult to explain the stabilizing effect obtained by acetylation as a protection of the β-O-4 aryl ether bond, since it has been suggested that most of the degradation of such bonds proceeds via cleavage of arylglycerol β-aryl ether structures (Fig. 7, Path A). The acetylation of γ-hydroxyl and phenolic hydroxyl groups could possibly influence the stability of the β-O-4 aryl ether bond and thereby retard the subsequent breakdown of these lignin units. Further work is needed to evaluate this possibility. Acetylation of the phenolic hydroxyl group in a lignin model compound of the 2-aryloxy-l-arylpropanone type could, however, not prevent the cleavage of the β-O-4 aryl ether structure upon irradiation (Hon 1995). This suggests that the phenacyl aryl ether pathway (Fig. 6) is still a possible source of phenoxyl radicals (and thereby chromophore formation) upon irradiation of acetylated high-yield pulps. A photo-Fries rearrangement, *i.e.*, homolytic cleavage of the ArO-$COCH_3$ bond, which releases the phenolic hydroxyl group and forms *ortho* and *para* rearrangement products, has been reported to occur upon photoyellowing of acetylated phenolic lignin model compounds (Braga and Hampp 2005) and could be one possible reason for the incomplete photostability obtained by acetylation. The cleavage of original 2-aryloxy-l-arylpropanone structures is probably responsible for only a small part of the total discoloration of high-yield pulps, since the number of such units in lignin is low compared with the number of phenolic hydroxyl groups. However, as can be seen in Fig. 7 (Path B), these structures could be generated from initially formed ketyl radicals and later give rise to new phenolic groups (phenoxyl radicals) by homolytic cleavage of the β-O-4 bond according to the phenacyl aryl ether pathway (Fig. 6). Further, it has been found that the content of noncondensed β-aryl ether units in bleached spruce thermomechanical pulp was essentially unchanged even after irradiation that caused an extensive brightness loss (Pan *et al*. 1992). It is worth mentioning that the monomeric thioacidolysis product coming from β-ethers only stems from noncondensed β-ether units. This means that a decrease in yield upon prolonged irradiation, reported by some, could be due to either β-ether cleavage and/or condensation reactions (Pan *et al*. 1992, 1993). On the contrary, the decrease in absolute amount of isolated dimeric thioacidolysis products after irradiation also points to a significant increase in the condensation degree (Pan *et al*. 1992).

The importance of cleavage of β-ethers for the formed color during photo-yellowing is probably minor; reactions involving arylglycerol β-aryl ether structures are less probable reaction pathways in chromophore formation during photoyellowing than reaction pathways involving photooxidation of free phenolic hydroxyl groups (Fig. 4 and

8), hydroquinones, catechols, or cleavage of 2-aryloxy-l-arylpropanone structures (Fig. 6), at least during the initial and most detrimental phase of photoyellowing. However, from a photostabilizing perspective, β-ether cleavage is more severe since it enables the formation of free phenols (source of phenoxyl groups), even if all free phenols are derivatized prior to ageing. The importance of structures that can initiate discoloration of lignin-containing pulps and participate in a cyclic process must also be taken into consideration. The significance of *o*-quinonoid compounds or some other still unknown structure needs to be investigated further.

Many photostabilizing treatments have been proposed, and some of the treatments are efficient in retarding discoloration. Although ultraviolet absorbers in combination with antioxidants have the potential to inhibit photoyellowing, the efficiency/cost ratio needs to be improved if these additives are going to be used. Derivatization of hydroxyl groups by chemical modification has been proven to be effective, but the deterioration in strength and optical properties and the technical difficulties in executing the chemical treatments in the pulp or paper mill makes chemical modification not a viable option. The best approach to protecting lignin-containing paper or board products against photo-yellowing is by coating them alone or with inhibiting additives. The use of fluorescent whitening agents could, at least for some time, slow down the discoloration. However, there exists today no photostabilizing treatment that is economically and/or technically feasible for a product in which the main part of the fiber material is of mechanical or chemimechanical origin.

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